



Site-specific quantitative ^2H NMR: A new tool for the assessment of contaminant fate in the subsurface

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Quantitative site-specific ^2H nuclear magnetic resonance (^2H NMR) measures the isotopic composition and relative distribution of deuterium (^2H) within contaminant molecules. Unlike conventional isotope ratio mass spectrometry (IRMS) that measures the isotopic composition ($^2\text{H}/^1\text{H}$) of the whole molecule, quantitative site-specific ^2H NMR allows one to compare the isotopic variation in $^2\text{H}/^1\text{H}$ within the molecule, based on different resonance peaks produced for each nucleus. The first objective of this study was to assess the accuracy and reproducibility of ^2H NMR analysis of a priority environmental contaminant, methyl *tertiary* butyl ether (MTBE). Calculated $\delta^2\text{H}$ values of the MTBE working standard, derived as weighted averages of ^2H NMR measurements of the two functional groups, showed good agreement with IRMS measurements attesting to the accuracy of the ^2H NMR technique ($\delta^2\text{H}$ of -105‰ versus -100‰ for ^2H NMR and IRMS measurements, respectively).

The second objective was to investigate the site-specific isotopic ratios of $^2\text{H}/^1\text{H}$ within MTBE to determine the potential of ^2H NMR measurements of the methoxy and *tertiary* butyl groups to provide an additional parameter for contaminant source forensic applications. The $\delta^2\text{H}$ of the methoxy group ranged from -103 to -171‰ while the *tertiary* butyl group ranged from -76 to -104‰ reflecting that they originate from methanol and isobutene, respectively. Several MTBE products whose whole-compound $\delta^{13}\text{C}$ and $\delta^2\text{H}$ MTBE values were within error of each other, as measured by IRMS, had demonstrably different $\delta^2\text{H}$ values for their methoxy and *tertiary* butyl groups measured by ^2H NMR. This provides proof in principle that quantitative ^2H NMR may provide an additional parameter for contaminant source forensics at field sites.

Finally, it was our goal to evaluate the influence than an uneven intramolecular distribution of isotopes would have on the isotopic fractionation of MTBE reported in previous studies. The measured isotopic variations in MTBE products were small enough not to bias the comparability of degradation-associated isotopic enrichment factors determined using different MTBE products. For example, the range in values calculated using the most extreme differences in ^2H isotopic distribution results in just a 4‰ difference in values of ε for biodegradation of MTBE.

Overall, our results suggest that the ability to gain accurate information about the site-specific isotopic ratios of $^2\text{H}/^1\text{H}$ within a molecule offers considerable promise as a new environmental technology to track the source and fate of environmentally problematic compounds in groundwater and soils.